Investigation of the non-linear properties and optical limiting capabilities of C_{60} and polyfluorene

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The non-linear properties of C_{60} and polyfluorene were investigated using the *z*-scan technique. C_{60} is a well-known optical limiter and its non-linear properties have been measured and documented. These measurements gave us an indication of the capabilities as well as the accuracy of our own experimental setup. Preliminary absorption measurements of polyfluorene indicated an unexpected time dependence.

Introduction

Optical limiters are used in a wide variety of applications, both military and commercial. The uses range from the protection of optical sensors such as the human eye to opto-electronic components such as optical switches.[1] Two quantities used to evaluate an optical limiter are 1) the non-linear index of refraction and 2) the non-linear absorption coefficient. The aim of the study reported here was to determine these properties of polyfluorene, using the *z*-scan technique. This method can be used to determine the non-linear absorption coefficient and has been described by Mansoor Sheik-Bahae *et al.*[2,3]

Theory

The principle of the *z*-scan is based on using a Gaussian laser beam in a tight focusing geometry, and moving the sample under investigation along the beam (along the *z*-axis) through the focal point (Fig. 1). The transmittance in the far field is measured and normalized to 1 for linear absorption, and plotted as a function of sample position along the *z*-axis, with the focus of the laser beam chosen to be at $z = 0$. The function that describes the normalized transmittance is given by the temporal integral[2]

$$T(z) = \frac{1}{\sqrt{\pi} q_0(z)} \int_{-\infty}^{\infty} \ln\left[1 + q_0(z) e^{-\tau^2}\right] d\tau \qquad (1)$$

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with

$$q_0 = \frac{\beta I_0 L_{eff}}{1 + z^2/z_0^2} \qquad (2)$$

and

$$L_{eff} = \frac{1 - e^{-\alpha L}}{\alpha}, \qquad (3)$$

where α is the linear absorption coefficient, L the optical path length through the sample, I_0 the on-axis intensity at the focus, z_0 the Rayleigh length and β the non-linear absorption coefficient. For $|q_0| < 1$, the normalized transmittance can be approximated to yield a form more suited to numerical calculations, namely

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}. \qquad (4)$$

This allows us to determine β unambiguously, by fitting the above formula to the experimental data obtained. From Equation (4), it follows that the approximation is valid only for transmittance >76.5%.

Experimental

Our investigations were conducted using an excimer pumped dye laser operating at 540 nm and a repetition rate of 10 Hz. All energy measurements were averaged over 100 shots. A 2 mM solution of C_{60} in toluene was prepared and analysed by means of a *z*-scan and the result is depicted in Fig. 2. The sample was moved in steps of 1 mm during the scan, using a beam energy of ~4 μJ. The on-axis intensity at the focus was determined by extracting the Rayleigh length from the fit to the data and using it to determine the beam waist. I_0 was found to be 4.3 MW cm^{-2}. The non-linear absorption coefficient for a 2 mM sample of C_{60} was determined to be 0.9 cm MW^{-1},which is in the same order of magnitude as extrapolation of results published by Couris *et al.*[1] suggests.

For the investigation of polyfluorene, a 2×10^{-10} M solution of the polymer in chloroform was prepared. When trying to determine the optimum energy with which to irradiate the sample (to obtain transmittance of ~80%), it was noticed that the absorption changed with time, which resulted in the asymmetrical shape of the *z*-scan. This phenomenon was investigated further.

For this investigation, the sample was placed at the focus of the *z*-scan setup and the transmittance, as a function of time rather than position, was recorded. Figure 3 depicts the transmittance of a sample irradiated over ~4500 s. Two *z*-scans of the sample after it had been irradiated for this time are displayed in Fig. 4. One scan was at the relatively low energy of ~7.5 μJ and the other at ~19.7 μJ, to determine whether the sample still acted as a non-linear absorber.

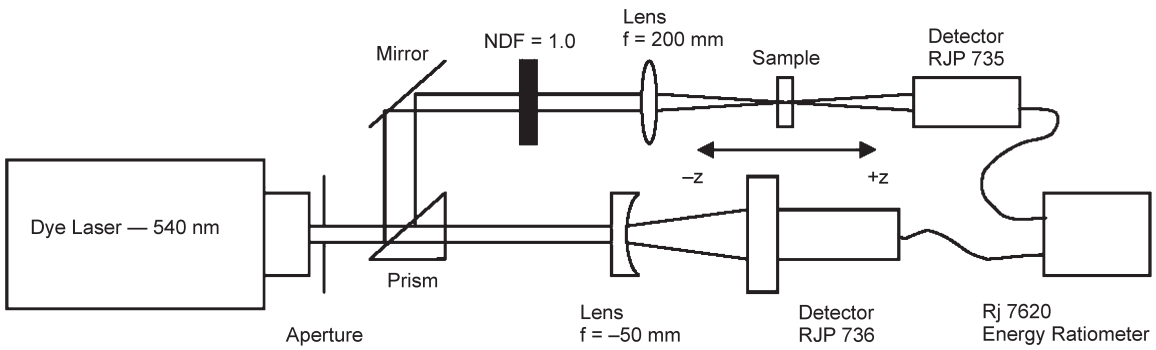

Fig. 1. The *z*-scan setup. The laser beam is split in two, one beam being used as the probe and the other as the reference. The ratio of the two beams is recorded with the energy ratiometer.

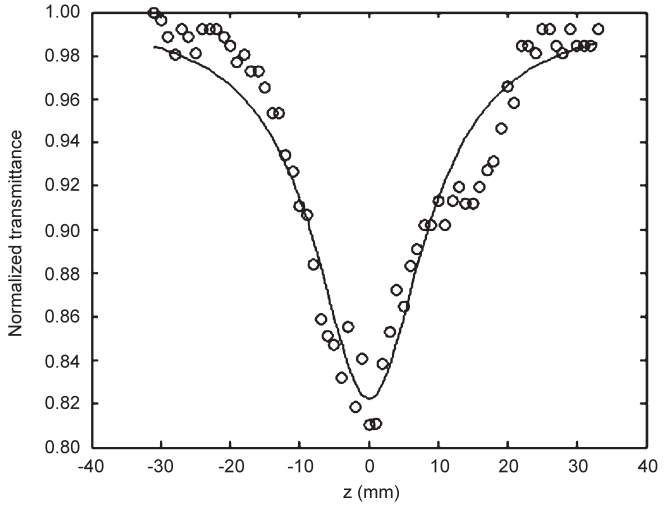

Fig. 2. A *z*-scan of C_{60} obtained using a dye laser at 540 nm and beam energy of 4 μJ. The continuous line corresponds to a least squares fit with β and z_0 as variable parameters. The Rayleigh length so obtained yielded the size of the waist, which enabled us to determine the on-axis intensity, I_0. This was found to be 4.3 MW cm^{-2}. The non-linear absorption coefficient was found to be 0.9 cm MW^{-1}.

Results and discussion

Figure 2 indicates that our *z*-scan setup gave reliable measurements and that the results obtained could be trusted. The unexpected time dependence of the absorption coefficient of polyfluorene, as depicted in Fig. 3, steered our investigation into a new direction. It was not possible to determine its non-linear properties because of this behaviour and so the time dependence was investigated further.

Figure 3 indicates that there were at least two competing processes taking place during the irradiation of polyfluorene. This was confirmed by the accuracy of the fit of two competing exponential functions on the data as shown in the figure. We suggest that the polymer was excited, possibly via a multi-photon process, into a state that had a higher absorption than originally. This intermediate state was then transformed, by absorbing radiation, into a state that did not display any non-linear absorption (as can be seen from the *z*-scan illustrated in Fig. 4 for the 'tempered' sample) and that is stable. Further experiments will be needed to determine the processes and time constants involved. Although we do not understand the changes that took place in the polymer over time, we speculate that the compound underwent a form of isomerization, where the new state was stable and did not display non-linear absorption, at least not at 540 nm.

Conclusions and future work

Our *z*-scan setup can be used to measure the non-linear absorption coefficient of C_{60}. We intend to automate the equipment, and believe we will be able also to measure the non-linear index of refraction of C_{60}. With this equipment we expect also to be able quickly and accurately determine the non-linear properties of any unknown absorbant sample.

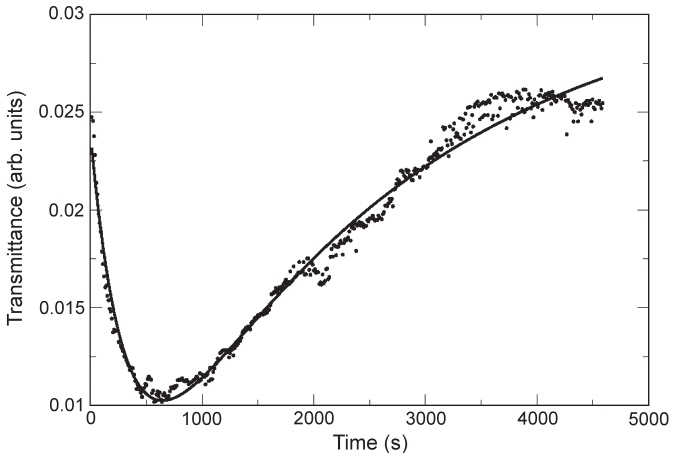

Fig. 3. A plot showing the transmittance of polyfluorene over a period of 4500 s. The function that was fitted was: $Ae^{-t/\tau_1} + B(1 - Ce^{-t/\tau_2})$. The two exponential terms seem to indicate that there were two competing processes involved.

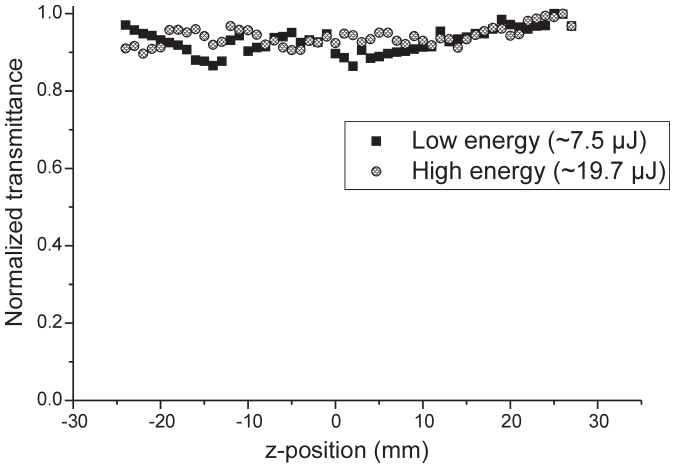

Fig. 4. Two *z*-scans of polyfluorene, after it had been irradiated for more than 4500 s at two different energies, clearly illustrating that it did not display non-linear absorption.

The time-dependent absorption of polyfluorene was possibly as a result of isomerization. We intend to investigate this behaviour further in an attempt to discover the processes involved.

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2. Sheik-Bahae M., Said A.A. and Van Stryland E.W. (1989). High-sensitivity, single-beam n_2 measurements. *Opt. Lett.* **14**(17), 955–957.
3. Sheik-Bahae M. *et al.* (1990). Sensitive measurement of optical nonlinearities using a single beam. *IEEE J. Quant. Electr.* **26**(4), 760–768.